

# PATENT SPECIFICATION

NO DRAWINGS

871.804



Date of Application and filing Complete Specification Feb. 4, 1958,

No. 3566/58.

Application made in Germany on Feb. 5, 1957.

Complete Specification Published June 28, 1961.

Index at acceptance:—Classes 1(1), A3B1; and 2(3), B11, B4A2, C3A13A(1A1:1L:3A1D:3A2:3B1:3B3:3L).

International Classification:—B01j, C07c, d.

## COMPLETE SPECIFICATION

### Improvements in the partial hydrogenation of Acetylene Compounds

We, BADISCHE ANILIN-&-SODA-FABRIK AKTIENGESELLSCHAFT, a Joint Stock Company, organised under the laws of Germany, of Ludwigshafen on Rhine, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the partial hydrogenation of acetylene compounds, more specifically to a process for the partial hydrogenation of acetylene compounds in the liquid phase in the presence of palladium catalysts.

The partial hydrogenation of triple linkages to ethylene linkages in organic substances has often been described. A comprehensive survey of the state of the art is to be found in Chem. Ind. Belg. 18 (1953), pages 1166 to 1178 (A. de Cat).

The catalysts normally used for this purpose are the conventional hydrogenation catalysts, such as nickel or palladium. These catalysts, in order that the particular purpose of a partial hydrogenation should be achieved, are weakened in their activity by the addition of special ingredients, such as alkalies, so that the triple linkages are hydrogenated, whereas the double linkages are hardly affected.

The activity of these catalysts is however only reduced to such an extent that olefinic linkages might also be hydrogenated if contact times considerably longer than those necessary for partial hydrogenation of the triple linkage were used. To prevent any such undesired hydrogenation the process is discontinued when a hydrogen equivalent has been absorbed for each triple linkage.

All these processes have the disadvantage that either the supply of hydrogen must be strictly regulated or, when the catalyst is strongly deactivated, the hydrogenation tem-

peratures must be raised. In this latter case, especially when high-boiling acetylene compounds are hydrogenated, the temperatures are raised to a level where appreciable losses in yield occur by side reactions, for example by the splitting off of acetylene or hydrogen.

We have now found that the partial hydrogenation of acetylene compounds can be directed so that the absorption of hydrogen comes to a complete standstill after the double linkage has been formed, by carrying out the hydrogenation in the presence of a palladium catalyst which has been treated with a salt of a metal of the groups IIb and/or IIIb of the Mendeleeff periodic system.

The palladium catalysts used in the practice of our invention can be made of finely divided palladium metal which has been obtained from palladium compounds, such as the oxides or salts, by reducing treatment, for example with hydrogen or formaldehyde, or by pyrolysis of organic palladium compounds.

The catalysts are prepared by treating a palladium metal of the type obtained in the said manner either by itself or applied to one of the known large-surfaced carriers, as for example calcium carbonate, barium carbonate, barium sulphate, active carbon or silica gel, with an aqueous or organic solution of a salt of a metal of the groups IIb and/or IIIb of the Mendeleeff periodic system. These metals of the groups IIb and IIIb of the Mendeleeff periodic system have the function of deactivators. Suitable deactivators of this type are zinc, cadmium, mercury, gallium, indium and thallium. The molar ratio of palladium catalyst to deactivator lies preferably between 0.01 and 1 mol of deactivator per 1 mol of palladium. The mol ratio, however, varies considerably. If zinc is used, for example, the mol ratio may be from 20:1 to 1:20. The deactivating action diminishes as

the atomic number of metals increases. There is therefore a considerable difference in the deactivating action between zinc and cadmium. Care must be exercised when adding cadmium, as cadmium may deactivate the catalyst completely. For the preparation of the catalysts, i.e. for precipitating the deactivators on the palladium metal, salts of these deactivator metals, in which the metals are contained as ions, are used. Especially suitable are the salts of hydrohalic acids, sulphuric acid, nitric acid, and also of organic acids, especially fatty acids, as for example formic acid, acetic acid, propionic acid, butyric acid, and higher fatty acids, also the salts of dicarboxylic acids, e.g. oxalic acid, malonic acid, succinic acid, or adipic acid. It is advantageous to use the water-soluble or alcohol-soluble salts of the said metals, for example zinc chloride, zinc sulphate, zinc nitrate, zinc formate, zinc acetate, sodium zincate, ammonium tetrachlorozincate, cadmium chloride, mercuric acetate, mercuric chloride, mercuric sulphate, mercuric acetamide and corresponding mercurous salts. Thallium (I) cyanide, thallium (II) chloride, thallium (III) nitrate, the corresponding salts of indium and gallium may also be used.

The metal salts can be deposited on the catalyst by precipitation or absorption. This treatment can take place before, during or after the reduction of the palladium catalyst. The catalysts can be used by themselves or precipitated on carriers.

The catalyst is preferably kept in a mobile state during the hydrogenation. In the usual case this can easily be effected by shaking the reaction vessel or by the leading in of the hydrogen.

The process in accordance with our invention can be used for the selective hydrogenation of all carbon triple linkages, the so-called acetylene linkages, i.e. the hydrogenation, when carried out by this process does not go further than to the carbon double linkage, the so-called ethylene linkage. The hydrogenation is selective, no matter what compound the carbon triple linkage is contained in.

The process is suitable both for the partial hydrogenation of simple acetylene compounds, as for example acetylene hydrocarbons, acetylene alcohols, acetylene glycols, acetylene amines, acetylene amino alcohols, acetylene carboxylic acids, which contain only one triple linkage to the corresponding ethylene compounds, and also for the selective and partial hydrogenation of compounds which contain, besides the acetylene linkage, also one or more other unsaturated olefinic or acetylenic gaseous acetylene compound can be bubbled through a mixture or suspension of the catalyst in a suitable solvent. In passing through the hydrogenation zone which preferably is a column of liquid the triple linkage of the

acetylene compound is completely hydrogenated.

It is preferable to add ammonia or a basic amine, e.g. a primary, secondary, or tertiary aliphatic amine, pyridine or quinoline, during the hydrogenation process. Ammonia may be added both in aqueous solution and in the gas phase. Quaternary ammonium salts in the presence of alkali may also be employed. In hydrogenating methyl butinol for instance it is advantageous to add a strongly basic amine, or preferably ammonia. In hydrogenating other compounds amines of lower basicity are added. Additions of even small quantities of amines produce satisfactory results. Often the addition of 0.0001 mol of amine to the acetylene compound to be hydrogenated is sufficient. Additions of considerably larger quantities of amines are not detrimental to the process. Amines may be added up to a molar ratio of acetylene compound to amine of 1 to 1, especially if the amine used simultaneously serves as a solvent. In this case the hydrogenation process can be carried out with amine in a large excess.

The hydrogenation can be carried out in the presence of water or organic solvents, for example alcohols, ethers or hydrocarbons. It is also possible however to hydrogenate in the absence of solvents.

The hydrogenation can be carried out within a wide temperature range, e.g. from 0° to 150° C; it is advantageous to work at room temperature or slightly elevated temperature, for example up to 80° C. The hydrogenation may be carried out either at normal pressure or at increased hydrogen pressure, for example up to 30° atmospheres. In many cases it is necessary to lead away by cooling the heat developed during the hydrogenation.

The absorption of hydrogen comes to a complete standstill after the calculated amount for the partial hydrogenation of the triple linkage has been reached. The end point of the partial hydrogenation may be ensured by exposing the reaction mixture for a few more hours to the hydrogenation conditions. No attack takes place on the double linkage formed or on any double linkages already present.

The following examples will further illustrate this invention but the invention is not restricted to these examples.

#### EXAMPLE 1

A palladium catalyst which contains 12 grams of palladium on 300 grams of calcium carbonate is stirred with a solution of 100 grams of zinc acetate in 500 grams of water and the mixture heated to boiling. It is filtered off and the catalyst dried in the air.

This catalyst is suspended in a mixture of 3,040 grams of 2,6-dimethyl-octene-2 in 7-

- ol-6, 5,000 grams of cyclohexane and 200 grams of pyridine in a stirring vessel. The suspension is treated with hydrogen, the absorption being measured with a gas meter.
- 9 The temperature is kept at 10° to 20° C. After about 490 litres of hydrogen have been absorbed, the whole is stirred for another 5 hours, no further absorption of hydrogen taking place.
- 10 The reaction product contains 3,080 of 2,6-dimethyl-octadiene-2,7-ol-6, i.e. about 100% of the theoretical yield. After filtering off the catalyst, the pure product of boiling point 95° C./20 mm is obtained by distillation.
- 15 The bromide absorption corresponds to the theoretical value. A triple linkage can no longer be detected. The catalyst recovered can often be used with constant results.

#### EXAMPLE 2

- 20 15 grams of the catalyst described in Example 1 are suspended in a mixture of 86 grams of butene-2-diol-1,4 and 240 grams of methanol. The mixture is treated with hydrogen, whereby it heats up to 30° to 40° C.
- 25 After the theoretical amount of hydrogen has been used up, the absorption ceases completely and the temperature falls.

- The reaction mixture contains 88 grams of butane-2-diol-1,4, i.e. about 100% of the theoretical yield. The reaction mixture is distilled and a practically quantitative yield of butene-2-diol-1,4 of boiling point 132° C./12 mm is obtained. This product is found to contain 97% of the cis-form and 3% of the transform by infra-red analysis.
- 35

#### EXAMPLE 3

- 30 grams of the catalyst described in Example 1 are suspended in 168 grams of 2-methyl-butene-3-ol-2 and 10 grams of quinoline and the mixture treated at 20° C. with hydrogen until no further absorption takes place. After distillation, 163 grams of 2-methyl-butene-3-ol-2 of boiling point 96—98° C./755 mm. are obtained, i.e. 95% of the theoretical yield.
- 40
- 45

#### EXAMPLE 4

- A palladium catalyst which contains 0.6 gram of palladium on 15 grams of calcium carbonate is suspended in 100 grams of water and stirred and heated to boiling with a solution of 0.9 gram of cadmium acetate in 50 grams of water. After filtering off and drying, the catalyst is suspended in a mixture of 250 grams of cyclohexane, 20 grams of pyridine and 152 grams of 2,6-dimethyl-octene-2-ine-7-ol-6, and the whole treated at 15° to 20° C. with hydrogen until 1 mol of hydrogen has been absorbed for each acetylene linkage. 154 grams of 2,6-dimethyl-octadiene-2,7-ol-6 are obtained (as described in Example 1), i.e. about 100% of the theoretical yield.
- 50
- 55
- 60

#### EXAMPLE 5

A palladium catalyst, which contains 6 grams of palladium on 150 grams of calcium carbonate, is stirred with a solution of 1 gram of mercuric acetate in 500 grams of water and heated to boiling. After filtering off and drying, this catalyst is mixed with 1,520 grams of 2,6-dimethyl-octene-2-ine-7-ol-6, 2,500 grams of cyclohexane and 100 grams of pyridine. The mixture is treated with hydrogen at 10° to 15° C. until no further absorption takes place. 1,540 grams of 2,6-dimethyl-octadiene-2,7-ol-6 are obtained (as described in Example 1), i.e. about 100% of the theoretical yield.

65

70

75

#### EXAMPLE 6

A palladium catalyst which contains 6 grams of palladium on 150 grams of calcium carbonate is treated with a solution of 1 gram of thallium trichloride in dilute hydrochloric acid while heating.

80

After filtering off and drying, the catalyst is used for hydrogenation of 1,520 grams of 2,6-dimethyl-octene-2-ine-7-ol-6 as described in Example 5.

85

In this case also, the absorption of hydrogen comes to a complete standstill after the supply of about 245 litres and the product is obtained as described in Example 1. The yield is almost quantitative.

90

#### EXAMPLE 7

0.3 kilogram of the catalyst described in Example 1 is suspended in 29.4 kilograms of 2-methyl-butene-3-ol-2 in a stirring vessel of 40 litres capacity. 0.06 kilogram of ammonia gas is led into the suspension. The mixture is treated at about 30° C. with hydrogen until for several hours no further absorption has taken place. About 8,500 litres of hydrogen are absorbed. After filtering off the catalyst, 2-methyl-butene-3-ol-2 is obtained by distillation (as in Example 3) in a quantitative yield.

95

100

#### EXAMPLE 8

15 grams of the catalyst described in Example 1 are added to a mixture of 137 grams of 3-piperidino-butene-1, 100 grams of methanol and 15 grams of piperidine and the whole shaken in a shaking vessel in an atmosphere of hydrogen until no further absorption takes place. The catalyst is then filtered off and the reaction product distilled. Pure 3-piperidino-butene-1 of the boiling point 47° to 48° C./8 mm. is obtained.

105

110

115

#### EXAMPLE 9

5 grams of the catalyst described in Example 1 are added to a solution of 26 grams of 1-ethinyl-cyclohexane-1 and 5 grams of piperidine in 100 grams of cyclohexane. The mixture is treated in a shaking vessel with hydrogen until no further absorption takes place. It is then filtered and fractionally dis-

120

tilled. Pure vinyl-cyclohexane-1 of boiling point 58° to 59° C./39 mm. is obtained.

#### EXAMPLE 10

5 grams of animal charcoal are added to a suspension of 1 gram of palladium in 100 grams of distilled water and treated with hydrogen while heating until saturation has taken place. The mixture is filtered and washed with water. The residue is treated while heating with a solution of 1 gram of cadmium acetate in 100 grams of water and filtered off.

The catalyst is suspended in 250 grams of 20% propargyl alcohol and shaken at 60° C. in a hydrogen atmosphere. The hydrogen absorption comes to a complete standstill after the calculated amount for the partial hydrogenation has been absorbed. The mixture is filtered. The bromine absorption of the aqueous allyl alcohol solution corresponds to the theoretical value.

#### EXAMPLE 11

300 grams of calcium carbonate are suspended in a solution of 140 grams of zinc acetate in 800 grams of water. While shaking vigorously there is added a solution of 20 grams of palladium chloride in 100 parts of water. The mixture is heated to 80° C. and treated with hydrogen while shaking until no further absorption takes place. The mixture is then kept at the boil for 30 minutes, filtered, and the residue dried *in vacuo* at 70° C.

A mixture of 29.5 kilograms of 2-methyl-butene-3-ol-2, 0.06 kilograms of ammonia, and 0.3 kilograms of the catalyst is treated with hydrogen in an autoclave at a hydrogen pressure of 20 atm. at 30° C. until the hydrogen absorption comes to a standstill. When the catalyst has settled down the clear conversion product is siphoned off. Neither 2-methyl-butene-3-ol-2 nor 2-methyl-butanol-2 can be traced in the conversion product. The yield of 2-methyl-butene-3-ol-2 is practically quantitative. The catalyst can be used about 20 to 30 times. With 0.3 kg of this catalyst 600 to 700 kilograms of pure 2-methyl-butene-3-ol-2 can be produced. Similar results are obtained if an equal amount of barium sulphate or finely ground activated carbon instead of calcium carbonate is used in preparing the catalyst.

#### EXAMPLE 12

654 grams of ethinyl-beta-ionol, obtained by reaction of beta-ionone with acetylene, are dissolved in 480 grams of methanol. 15 grams of the catalyst described in Example 1 and 0.6 grams of an 0.5 normal methanolic ammonia solution are added and the mixture treated with hydrogen at room temperature under atmospheric pressure. The hydrogen absorption comes to a standstill when the quantity calculated for the hydrogenation of

the ethinyl group into the vinyl group has been absorbed. The catalyst is filtered off and the reaction mixture distilled. 634 grams of vinyl-beta-ionol of boiling point 82° C./0.4 mm. are obtained.

#### EXAMPLE 13

A mixture of 660 grams of isopropenyl acetylene, 30 grams of methylamine, and 20 grams of the catalyst described in Example 5 are treated with hydrogen in a stirring flask at room temperature while shaking until the hydrogen absorption comes to a standstill. The catalyst is filtered off by suction and the mixture distilled, 620 grams of pure isoprene of boiling point 34° C./755 mm. being obtained.

#### EXAMPLE 14

A mixture of 1,000 grams of butene-2-diol (1.4) and 150 grams of the catalyst described in Example 1 are treated with hydrogen at 80° C. and 100 atmospheres in a pressure vessel which is provided with a stirrer until the absorption comes to a standstill. The cold reaction mixture is filtered off from the catalyst by suction and distilled fractionally. There are obtained 920 grams of pure butene-diol of boiling point 132° C./12 mm. and 80 parts of a resinous residue.

#### EXAMPLE 15

1 gram of palladous chloride is dissolved in 100 grams of distilled water and heated to 80° C. The warm solution is treated with hydrogen until the palladium salt is completely reduced. The suspension is filtered and the wet catalyst added to a solution of 5 grams of zinc acetate in 150 grams of distilled water. This mixture is heated for 10 minutes (bringing to the boil), filtered and washed several times with methanol.

The catalyst thus prepared is suspended in 84 grams of 2-methyl-butene-3-ol-2, 2 grams of a 33% methylamine solution are added to the mixture and the mixture treated with hydrogen in a shaking autoclave at a hydrogen pressure of 20 atm. After the absorption of 1 equivalent of hydrogen the hydrogenation process comes to a complete standstill. By distillation there is obtained pure 2-methyl-butene-3-ol-2 of boiling point 96–98° C./755 mm.

The British Patent Specification No. 804,788 claims a catalyst which comprises as essential catalytic components palladium sponge deposited on a substrate comprising a mixture of zinc and iron hydroxides and/or zinc and iron carbonates (including basic carbonates); the gram atomic proportion of palladium to zinc and iron being of the order of 2 to 9 of palladium to 1 of zinc and 1 of iron, and we make no claim to such a catalyst or its use. Subject to the foregoing disclaimer what we claim is:—

1. A process for the partial hydrogenation

- of acetylene compounds wherein the hydrogenation is carried out in the presence of a palladium catalyst which has been treated with an aqueous or organic solution of a salt of a metal of the groups IIb and/or IIIb of the Mendeleeff periodic system.
- 5 2. A process as claimed in Claim 1 wherein the catalyst is applied to a carrier.
- 10 3. A process as claimed in Claim 1 or 2 wherein the hydrogenation is carried out in the presence of a solvent.
4. A process as claimed in any of Claims 1 to 3 wherein the hydrogenation is carried out in the presence of an amine.
- 15 5. A process for the partial hydrogenation of acetylene compounds substantially as described in any of the foregoing examples.
6. Compounds containing double linkages when obtained by the process claimed in any of Claims 1 to 4. 20
7. As a new composition of matter a palladium catalyst for use in hydrogenation processes which has been treated with an aqueous or organic solution of a salt of a metal of the groups IIb and/or IIIb of the Mendeleeff periodic system. 25
8. As a new composition of matter a catalyst as claimed in Claim 7 applied to a carrier.

J. Y. & G. W. JOHNSON,  
47, Lincoln's Inn Fields,  
London, W.C.2,  
Chartered Patent Agents.